STUDIES ON LANTHANUM AND CHROMIUM DOPED ZnO THIN FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

A synopsis submitted

To

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1. Introduction

The semiconductor industry has experienced tremendous growth as a result of peoples depend on its products in their everyday lives. Progress requires the creation of ever-smaller devices that are faster, more flexible, perform better, and are less expensive. As a result of this need, new technologies and materials have been developed to fulfil the needs of the developing semiconductor industry. Nanotechnology is one of the most recent and active areas of study, in which devices include very small particles and exhibit unique features. Thin-film technology, which permits the deposition of very thin layers of semiconductor material on a supporting substrate plays a significant role in this respect.

Metal oxide semiconductors (MOSs) thin films have been employed in a variety of applications, including near-UV light emitting diodes (LEDs), gas sensors, solar cells, nonvolatile memory, and optoelectronic devices due to its wide band gap [1]. Furthermore, semiconductors thin films have acquired significant importance in recent years due to their distinct electrical and optical characteristics when doped with metal atoms. Among several metal oxides semiconductors, ZnO is a well-known transparent and conductive material because of its unique properties such as, large band gap (3.37 eV), a high excitonic energy (60 meV) at room temperature, low resistivity, good thermal, mechanical and chemical stability [2]. Also, ZnO is a promising material since it is nontoxic, abundant, relatively inexpensive and easy to prepare.

Doping is the most effective technique to increase the structural, optical and electrical properties of the pure form material since the dopants may change the energy band structure, morphology and surface to volume ratio, create more active centers at grain boundaries and produce defects and vacancies ruthenium (Ru), Erbium (Er), cesium (Ce) and transition metals including nickel (Ni), manganese (Mn), iron (Fe), cobalt (Co), titanium (Ti), and magnesium (Mg) have been shown to be effective dopants for ZnO in a variety of applications [3-4]. In comparison to the above-mentioned elements, La and Cr is often doped into ZnO matrix to alter its optical, electrical, and ferromagnetic characteristics [5], but it has not been widely used in gas sensing applications till now. Lanthanum (La), which has largest ionic radius (1.032Å), has significant ability to modify the crystal structure of ZnO by adding extra defects into the host material [6]. Furthermore, Cr^{3+} has close ionic radius to Zn^{2+}, and can be substituted easily to the ZnO lattice. [7].

In the proposed work we will prepare good quality of undoped ZnO, La-doped and Cr-doped ZnO thin films via spray pyrolysis method.

2. Review of Literature

In the literature there is lot of work has been done on transition metal doped ZnO thin films to improve the structural optical, magnetic and electrical properties. Nevertheless, only few studies reported about the La-doped ZnO and Cr-doped ZnO thin films.

- **J. Santhosam et. al**. [8] reported La-doped ZnO gas sensor prepared by spray pyrolysis technique. They found that 3% La-doped ZnO sensor shows highly sensitive with fast response and recovery time towards the ammonia gas.
- **A. Gozeh et. al.** [9] studied structural, optical and electrical properties of La-doped ZnO thin films prepared by solgel method. They found IV characteristics parameters such as barrier height, ideality factor and series resistance were enhanced after the La doping.
- **Ayana et al.** [10] revealed the enhancement of optical limiting performance of La^{3+} doped ZnO thin films prepared by spray pyrolysis technique. The study shows the films with 3% doping concentration has least crystallite size with maximum dislocation density. Also, morphology changed from fibrous to needle like structure with increased dopant concentration.
- **Abhishek Ghosh et. al.** [11] investigated highly sensitive hydrogen gas sensor using La-doped ZnO thin films by sol-gel method at operating temperature of 300^0 C. In their work they found that 5 at% La-doped ZnO thin films shows higher sensitivity towards the hydrogen gas for a 10-500ppm.
- **K. Shingange et. al.** [12] demonstrated La-doped ZnO nanofiber for H_2S gas sensor as the effect of post annealing at various doping levels. The study reveals that 2wt% doping annealing at 900^0C shows the highest H_2S response at an optimum operating temperature of 175^0C with good repeatability and stability.
- **P. Nakarungsee et. al.** [13] synthesized Cr doped ZnO nanoparticle by Hydrothermal method for Ammonia gas sensing tested under UV illumination at room temperature. The results showed that irradiated Cr doped ZnO nanoparticles have higher gas sensitivity towards ammonia gas of concentration 50 ppm at room temperature than that of undoped ZnO nanoparticles.

- **I. Y. Habib et. al.** [14] investigated the ZnO and Cr-doped ZnO nanostructures by sol-gel method for CO sensor and found that the enhanced gas sensing performance with Cr doped films and the sensitivity increased from 9.65% to 64.45% and simultaneously the decreased the response and recovery time from 334.5 s to 172.3 s and 219 s to 37.2 s respectively.
- **M. M. Hassan et. al.** [15] demonstrated the enhancement of ethanol sensitivity of Cr-doped ZnO thin films prepared by RF sputtering on Al_2O_3 substrate. The Cr doping enhanced the sensitivity of ZnO sensor almost twice and also improved the response time and recovery time, which was due to the increase in surface in surface to volume ratio which leads to adsorption of a greater number of ethanol gas molecules.
- **A. K. Worku et. al.** [16] synthesized pure ZnO and Cr-doped ZnO nanoparticles via chemical co-precipitation route and their structural, thermal characteristics were discussed systematically. They studied the effect of variation Cr doping concentration from 0.05 M to 0.1M and calcined at 600^0C. The prepared samples were analyzed via XRD, FTIR etc. revealed the average particle sizes between 23 to 39nm. Also, the study showed the increased surface area and thermal stability with increasing Cr concentration.
- **G. Mangamma et. al.** [17] Prepared nanostructured pure and Chromium doped ZnO thin films on glass substrate by spin coating technique. They investigated the structural, optical, and electrical properties by XRD, UV-visible spectroscopy, scanning electron microscope, Raman Spectroscopy and IV measurements. The results showed that the particle size decreased with variation in Cr concentration. Also, lattice parameter, bond length and average particle size has been determined from XRD data.

3. Statement of proposed problem

La and Cr is often doped into ZnO matrix to alter its optical, electrical, and ferromagnetic characteristics, but there are very few reports are available on gas sensing applications till now. So, the propose of work is planned to prepare La and Cr-doped ZnO thin films and study the influences of doping on its characteristics. Further, as most of the ZnO thin films sensors are operate at the operating temperature that are above the 200^oC, which heat the sensor device. This problem decreases the life time and long-term stability of the sensor. Attempt will made to overcome such problems by doping the ZnO with transition metal as well as rare earth element.

4. Objective of proposed work

- To prepare thin films of pure ZnO thin films, La-doped ZnO and Cr-doped ZnO thin films by cost effective spray pyrolysis technique.
- To investigate the structural properties, morphological, optical, electrical and gas sensing properties of undoped, La-doped and Cr-doped ZnO thin films.

5. Motivation

Thin films have drastically different characteristics than their bulk materials. Thin films based on semiconductor metal oxides (SMOs) have been extensively used due to their distinct optical and electrical properties. Among all the SMOs, zinc oxide (ZnO) is one of the first choice SMOs due to its unique properties such as large band gap (3.37 eV), a high excitonic energy (60 meV) at room temperature, low resistivity, good thermal, mechanical and chemical stability. Further when ZnO is doped with suitable dopant its structural, morphological, optical, electrical as well as gas sensing properties enhanced. Such types of films then considered as one of the prominent candidates in various of applications like light emitting diode (LED), solar cell, piezoelectric devices, gas sensor, spintronic devices, photo detector, laser diodes etc.

6. Hypothesis/ Assumption

- The research work is directed to obtain new and improved pure ZnO and La and Cr-doped ZnO thin films.
- The enhancement in morphological and optical properties of pure ZnO thin films after the La and Cr-doping will be expected.
- The sensing performance like selectivity, sensitivity, response and recovery time of SMOs films will improve with doping.

7. Research Methodology

Thin films preparation

It is well known that the pure and doped ZnO thin films can be deposited by various chemical and physical method such as thermal evaporation, pulsed laser deposition, sputtering, chemical bath deposition, spin coating, SILAR, spray pyrolysis, solgel and molecular beam epitaxy. Among all, in the proposed work we use spray pyrolysis technique due to its adequate advantages like low cost, easy control of chemical uniformity, better stoichiometry control, easier fabrication of large area films and purity

Characterization

Structural characterization: X-ray diffraction (XRD) is used for two reasons: first it provides information about the crystallographic properties of the materials. Secondly, it can be used to determine Structural parameters.

Morphological characterization: The scanning electron microscope (SEM) is one of the most useful and versatile instruments for the investigation of surface topography, micro-structural features, etc.

Energy dispersive X-ray analysis (EDX) is used to identify and the relative compositions of elements of samples.

Optical absorption spectrometry Measurement: Optical absorption spectrometry is a very important tool to study the optical band gap of the films. Optical absorption measurements of the thin films will be carried out at room temperature in the wavelength range of 200 to 800 nm using the UV-VIS spectrophotometer.

Gas sensing Studies: The gas sensing performance of the prepared sensor will study using home-made device with a high resistance electrometer.

8. Chapter Scheme

Chapter 1: Introduction and Literature review

Chapter 2: Experimental methods and Characterization techniques

Chapter 3: Study of Undoped ZnO thin Films, La-doped and Cr-doped ZnO thin films

Chapter 4: Application based study of Undoped ZnO thin Films, La-doped and Cr-doped ZnO thin films

Chapter 5: Conclusions and future work plan

9. Year wise plan of work and targets

First year

In first six months, will complete Course work and after Six months will do literature review on pure and doped ZnO thin films prepared by spray pyrolysis method. Preparation and characterization of pure ZnO thin films, La-doped ZnO from spray pyrolysis technique.

Second year

In the second year we will deposit thin films of Cr-doped ZnO and we will do characterization by XRD, SEM, EDAX, UV-VIS and gas sensing. Also, we will prepare research papers and publish it in reputed journals for publication.

Third year

In the third year we will publish research paper in reputed journals also, the outcomes of our research work will be presented in national and international conferences, seminars etc. Finally, we will write thesis for the Doctoral degree.

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